

# Melting of alloys along the inter-phase boundaries in eutectic and peritectic systems

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We discuss a simple model of the melting kinetics along the solid-solid interface in eutectic and peritectic systems. The process is controlled by the diffusion inside the liquid phase and the existence of a triple junction is crucial for the velocity selection problem. Using the lubrication approximation for the diffusion field in the liquid phase we obtain scaling results for the steady-state velocity of the moving pattern depending on the overheating above the equilibrium temperature and on the material parameters of the system, including the dependences on the angles at the triple junction.

## I. INTRODUCTION

The systematic investigation of melting kinetics in alloys, and particular in eutectic and peritectic systems, is much less developed than the investigation of solidification (for a recent review on solidification see, for example [1] and references therein). Microstructures, being at the center of materials science and engineering, are formed during the solidification process and, in this sense, the melting process is less attractive for practical applications.

However, the interfacial pattern selection problem during the melting process might be very interesting. For example, in our previous publications [2, 3] we discussed a free boundary problem for two moving interfaces that strongly interact via the diffusion field in the liquid layer between them. This problem arises in the context of liquid film migration during the partial melting of solid alloys [4] and could also be relevant to the sintering process in the presence of the liquid phase [5]. For the melting of one-phase alloys to proceed in this way, the local equilibrium concentrations have to be different for the two interfaces providing the driving force for the process. It is by now well accepted (see, for example, [6, 7]) that the difference of the equilibrium states at the melting and solidification fronts is due to the coherency strain energy which is important only at the melting front because of the sharp concentration profile ahead the moving melting front.

The other source of elastic deformations during the melting process, even in pure materials, is the density difference between the solid and the liquid phase. If the melt inclusion is entirely inside the solid matrix, inhomogeneous elastic deformations inevitably arise. The peculiar behavior of the melting kinetics in such systems was discussed in [8, 9].

The main purpose of this paper is to describe the problem of contact melting in eutectic and peritectic systems along the boundary between two solid phases (see Fig. 1 and Fig. 2). The local concentrations at the  $L/\alpha$  and  $L/\beta$  interfaces in such systems are different because of the chemical difference between the  $\alpha$  and  $\beta$  phases, and weak coherency strain effects are not so important here. If we also assume that the liquid phase extends up to

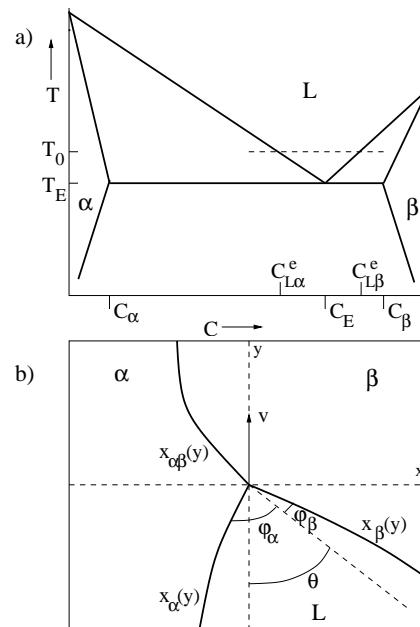


FIG. 1: Schematic presentation of the phase diagram a) and configuration of different interfaces near the triple junction b) in eutectic systems.  $x_{\alpha\beta}(y)$  is the interface between two solid phases  $\alpha$  and  $\beta$ ; the interfaces between the liquid phase  $L$  and the solid phases are denoted by  $x_\alpha(y)$  and  $x_\beta(y)$ . In the steady state regime this configuration moves along the  $y$  axis with a constant velocity  $v$ . The origin of the coordinate system is located at the triple junction.

the sample surfaces, the mentioned elastic deformations due the density difference are not important either, because a weak hydrodynamic flow inside the liquid phase compensates the density difference.

We concentrate here on the velocity selection problem during the melting along the solid-solid interface. The presence of the triple junction (see Fig.1b and Fig. 2b) plays a crucial role in this process. In the classical problem of dendritic growth, where the triple junction is not present, the velocity selection is controlled by tiny singular effects of the anisotropy of the surface energy (for review see [10, 11]). The triple junction produces a very strong perturbation of the liquid-solid interfaces

and controls the velocity selection. The other important difference compared to the classical dendritic problem is that the kinetics of the contact melting in eutectic and peritectic systems is controlled by the diffusion inside the needle-like liquid phase and not in the outer phase.

All features of the contact melting process mentioned so far are common for both systems. There is, however, important difference between eutectic and peritectic systems. In the eutectic system (Fig. 1) both interfaces  $L/\alpha$  and  $L/\beta$  are melting fronts while in the peritectic system (Fig.2) the  $L/\alpha$  interface is a solidification front if the temperature  $T_0$  is above the peritectic temperature  $T_p$ . In other words, during the melting of peritectic systems the low-temperature  $\beta$ -phase melts while the high-temperature  $\alpha$ -phase solidifies. It means that, additionally to the formation of the liquid phase, the polymorphic transition  $\beta \rightarrow \alpha$  occurs. In this context the contact melting in the peritectic system is similar to the process of liquid film migration, mentioned above, where the liquid film is also located between melting and solidification fronts.

Finally, we discuss in this paper the evolution of the solid-solid interface due to surface diffusion. This process inevitably arises due to the deviation of the interface from a flat configuration in the vicinity of a triple junction. We show, however, that surface diffusion does not play a controlling role in the melting kinetics, and only allows for the necessarily adjustment of the solid-solid interface.

## II. ISOTHERMAL MELTING IN EUTECTIC SYSTEM

We consider the two-dimensional problem of the simultaneous melting of two eutectic phases  $\alpha$  and  $\beta$  along the boundary between them. The phase diagram and the configuration of different interfaces near the triple junction are schematically presented in Fig.1. The compositions of the solid phases are close to their equilibrium values  $C_\alpha$  and  $C_\beta$  at the eutectic temperature. We assume that diffusion in the solid phases is very slow. The temperature of the sample,  $T_0$ , is slightly above the eutectic temperature  $T_E$  (for the notations see Fig.1). At small overheating the concentration field in the liquid,  $C(x, y)$  obeys the Laplace equation

$$\Delta C = 0. \quad (1)$$

We assume local equilibrium at the liquid-solid interfaces. Then the concentrations at the  $L/\alpha$  and  $L/\beta$  interfaces are:

$$\begin{aligned} C_{L\alpha}(y) &= C_{L\alpha}^e + (C_\beta - C_\alpha)d_\alpha x_\alpha''(y), \\ C_{L\beta}(y) &= C_{L\beta}^e + (C_\beta - C_\alpha)d_\beta x_\beta''(y). \end{aligned} \quad (2)$$

Here the notations of the different concentrations are clear from the phase diagram (Fig. 1a); the capillary lengths are

$$d_{\alpha(\beta)} = \frac{\sigma_{\alpha(\beta)}\Omega}{|C_E - C_{\alpha(\beta)}|(C_\beta - C_\alpha)f_L''(C_E)},$$

where  $\sigma_{\alpha(\beta)}$  is the surface energy of the  $L/\alpha(\beta)$  interface,  $\Omega$  is atomic volume which is assumed to be the same in all three phases,  $f_L(C)$  is the free energy of the liquid phase per atom and  $f_L''(C)$  is its second derivative with respect to  $C$ . The mass balance conditions at these interfaces read:

$$\begin{aligned} D\partial C/\partial x &= v(C_E - C_\alpha)x'_\alpha(y), \\ D\partial C/\partial x &= -v(C_\beta - C_E)x'_\beta(y), \end{aligned} \quad (3)$$

where  $D$  is the diffusion coefficient in the liquid phase.

Eqs. (2)-(3) are written for the case of small angles  $\theta$ ,  $\varphi_\alpha$  and  $\varphi_\beta$  at the triple junction. This leads to the small angles along the whole interface,  $x'_\alpha \ll 1$  and  $x'_\beta \ll 1$ . In this case we can use the so-called “lubrication” approximation for the solution of the Laplace equation. In this approximation one neglects the derivatives with respect to the “slow”  $y$  variable as compared with the derivatives with respect to the “fast”  $x$  variable:

$$C(x, y) = C_0(y) + B(y)x. \quad (4)$$

The slow variable functions  $C_0(y)$  and  $B(y)$  can be found from the boundary condition, Eq. (2):

$$\begin{aligned} C_0(y) &= \frac{C_{L\alpha}(y)x_\beta(y) - C_{L\beta}(y)x_\alpha(y)}{x_\beta(y) - x_\alpha(y)}, \\ B(y) &= \frac{C_{L\beta}(y) - C_{L\alpha}(y)}{x_\beta(y) - x_\alpha(y)}. \end{aligned} \quad (5)$$

From Eqs. (3) and (4) we find the following relations,

$$x'_\alpha = \frac{D}{v} \frac{B(y)}{(C_E - C_\alpha)}, \quad x'_\beta = -\frac{D}{v} \frac{B(y)}{(C_\beta - C_E)}, \quad (6)$$

which together with Eqs. (5) and (2) form a closed system of two second order differential equations for the front profiles  $x_\alpha(y)$  and  $x_\beta(y)$ . They are subject to the boundary conditions at the triple junction:

$$x_\alpha(0) = x_\beta(0) = 0, \quad (7)$$

$$x'_\alpha(0) = \varphi_\alpha - \theta \equiv \theta_\alpha; \quad x'_\beta(0) = -(\varphi_\beta + \theta) \equiv -\theta_\beta \quad (8)$$

(see Fig. 1b). It follows from Eqs. (6) and (7) that

$$x_\alpha(y) = -gx_\beta(y), \quad (9)$$

where  $g = (C_\beta - C_E)/(C_E - C_\alpha)$ . We also find from Eq. (8) that

$$\theta_\alpha = \frac{g(\varphi_\alpha + \varphi_\beta)}{1+g}, \quad \theta_\beta = \frac{\varphi_\alpha + \varphi_\beta}{1+g}, \quad \theta = \frac{\varphi_\alpha - g\varphi_\beta}{1+g}. \quad (10)$$

The relation (9) allows to eliminate the profile  $x_\alpha$  and to write the closed equation for the profile  $x_\beta$ . Moreover, one can integrate this equation once with respect to  $y$  and

finally obtains a nonlinear first order differential equation for the profile  $x_\beta$ :

$$-(d_\beta + gd_\alpha)x'_\beta = (d_\beta + gd_\alpha)\theta_\beta + \Delta y + \frac{vg}{2D}x_\beta^2. \quad (11)$$

Here  $\Delta = (C_{L\beta}^e - C_{L\alpha}^e)/(C_\beta - C_\alpha)$  is the dimensionless overheating above the eutectic temperature.

Let us introduce the dimensionless coordinates:

$$X_\beta = \frac{x_\beta \Delta}{\theta_\beta^2(d_\beta + gd_\alpha)}, \quad Y = \frac{y \Delta}{\theta_\beta(d_\beta + gd_\alpha)}. \quad (12)$$

Then Eq. (11) takes the form

$$-X'_\beta = 1 + Y + \nu X_\beta^2 \quad (13)$$

with the dimensionless parameter  $\nu$ :

$$\nu = v \frac{g(d_\beta + gd_\alpha)\theta_\beta^3}{2D\Delta^2}. \quad (14)$$

The solution of this equation starts at the origin with  $X'_\beta(0) = -1$  and should have parabolic asymptotics  $X_\beta = \sqrt{|Y|/\nu}$  for large values of  $|Y|$ . It turns out that such a smooth solution exists only if the parameter  $\nu = \nu^* \approx 1.06$ . In other words, this is a nonlinear eigenvalue problem which leads to the selection of the velocity  $v$ :

$$v = \nu^* \frac{2D\Delta^2}{g(d_\beta + gd_\alpha)\theta_\beta^3} \quad (15)$$

We see that the posed problem has a relatively simple, essentially analytical solution.

### III. ISOTHERMAL MELTING IN PERITECTIC SYSTEM

The phase diagram and the configuration of different interfaces near the triple junction are schematically presented in Fig. 2. The temperature of the sample is  $T_0$  and slightly above the peritectic temperature  $T_P$  (for the notations see Fig. 2a). Overheating is assumed to be small and the compositions of the solid phases are close to the equilibrium values  $C_\alpha$  and  $C_\beta$  at the peritectic temperature. Eqs. (1)-(3) are valid also for the peritectic system where  $C_E$  should be replace by  $C_P$  and in the second equation in (2) one should change the sign in front of the capillary term,

$$C_{L\beta}(y) = C_{L\beta}^e - (C_\beta - C_\alpha)d_\beta x''_\beta(y).$$

This reflects the fact that the equilibrium between the  $\beta$ -phase and the liquid phase corresponds to the negative slope of the liquidus line for the peritectic phase diagram and to the positive slope for the eutectic diagram. As a result, Eqs. (9)-(10) remain the same and Eq. (11) is replaced by

$$-(d_\beta - gd_\alpha)x'_\beta = (d_\beta - gd_\alpha)\theta_\beta - \Delta y - \frac{vg}{2D}x_\beta^2. \quad (16)$$

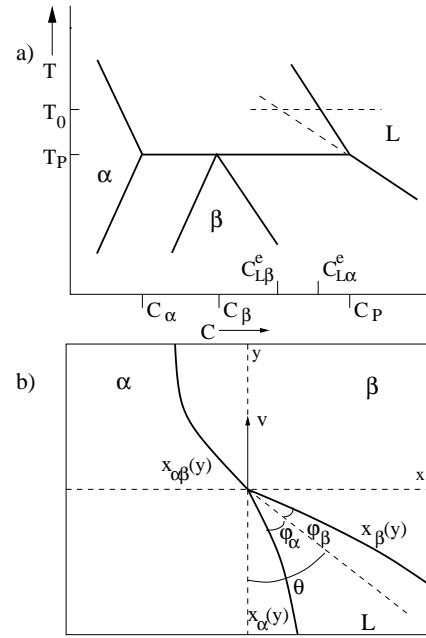


FIG. 2: Schematic presentation of the phase diagram a) and configuration of different interfaces near the triple junction b) in peritectic systems.  $x_{\alpha\beta}(y)$  is the interface between two solid phases  $\alpha$  and  $\beta$ ; the interfaces between the liquid phase  $L$  and the solid phases are denoted by  $x_\alpha(y)$  and  $x_\beta(y)$ . In the steady state regime this configuration moves along the  $y$  axis with a constant velocity  $v$ . The origin of the coordinate system is located at the triple junction.

We note that the parameters  $g$  and  $\Delta$  for the peritectic system (Fig. 2) are negative if we define them in the same way as for the eutectic system:

$$g = (C_\beta - C_P)/(C_P - C_\alpha), \quad \Delta = (C_{L\beta}^e - C_{L\alpha}^e)/(C_\beta - C_\alpha)$$

Thus, replacing  $-g$  by  $|g|$  and  $-\Delta$  by  $|\Delta|$ , we recover Eq. (13) with

$$X_\beta = \frac{x_\beta |\Delta|}{\theta_\beta^2(d_\beta + |g|d_\alpha)\theta_\beta^3}, \quad Y = \frac{y |\Delta|}{\theta_\beta(d_\beta + |g|d_\alpha)\theta_\beta^3} \quad (17)$$

and

$$\nu = v \frac{|g|(d_\beta + |g|d_\alpha)\theta_\beta^3}{2D\Delta^2}, \quad \theta_\beta = \frac{\varphi_\alpha + \varphi_\beta}{1 - |g|}. \quad (18)$$

Finally, for the steady-state velocity we obtain

$$v = \nu^* \frac{2D\Delta^2}{|g|(d_\beta + |g|d_\alpha)\theta_\beta^3} \quad (19)$$

As we have already noted in the Introduction, the interface  $x_\alpha = |g|x_\beta$  represents now a solidification front. During the melting, in the peritectic system, the low-temperature  $\beta$ -phase melts while the high-temperature  $\alpha$ -phase solidifies. In addition to the formation of the liquid phase the polymorphic transition  $\beta \rightarrow \alpha$  takes place.

#### IV. EVOLUTION OF THE SOLID-SOLID INTERFACE

We have already mentioned that diffusion along the solid-solid interface plays an important role allowing the necessary rotation of the structure in the vicinity of the triple junction,  $x'_{\alpha\beta}(0) = -\theta$  (see Fig. 1b and Fig. 2b). At the same time, far away from the triple junction, the solid-solid interface is parallel to the  $y$  axis ( $x'_{\alpha\beta}(\infty) = 0$ ).

The corresponding surface diffusion equation which describes the  $x_{\alpha\beta}(y)$  interface has been discussed in [12] and, essentially, it is given by the classical Mullins equation [13]:

$$2\delta_{\alpha\beta}d_{\alpha\beta}D_{\alpha\beta}\frac{d^4x_{\alpha\beta}}{dy^4} - v\frac{dx_{\alpha\beta}}{dy} = 0 \quad (20)$$

In this description the diffusion takes place inside of layer of the thickness  $2\delta_{\alpha\beta}$  (diffusion coefficient is  $D_{\alpha\beta}$ ) and  $d_{\alpha\beta}$  is the corresponding capillary length:

$$d_{\alpha\beta} = \frac{\sigma_{\alpha\beta}\Omega[f''_{\alpha}(C_{\alpha}) + f''_{\beta}(C_{\beta})]}{2(C_{\beta} - C_{\alpha})^2f''_{\alpha}(C_{\alpha})f''_{\beta}(C_{\beta})}.$$

Here  $f_{\alpha(\beta)}(C)$  is the free energy of the  $\alpha(\beta)$  phase per atom. The solution of this equation which has a proper behavior at large values of  $y$  and satisfies the boundary conditions  $x_{\alpha\beta}(0) = 0$ ,  $x'_{\alpha\beta}(0) = -\theta$  and  $x''_{\alpha\beta}(0) = \kappa(0)$ , is

$$x_{\alpha\beta}(y) = A - \exp\left(-\frac{qy}{2}\right)[A\cos(\frac{qy\sqrt{3}}{2}) + B\sin(\frac{qy\sqrt{3}}{2})],$$

$$A = [\kappa(0)/q - \theta]/q; \quad B = [\kappa(0)/q + \theta]/(q\sqrt{3}), \quad (21)$$

where  $q^3 = v/(2\delta_{\alpha\beta}d_{\alpha\beta}D_{\alpha\beta})$ . This solution is uniquely defined because the parameters  $v$ ,  $\theta$  and  $\kappa(0)$  are known from the solution given in the previous sections. The velocity is given by Eqs. (15) and (19) for the eutectic and peritectic systems respectively; the angle  $\theta$  is given by Eq. (10) for both cases and the curvature of the  $\alpha/\beta$  interface at the triple junction,  $\kappa(0) \sim \Delta/d_{\alpha\beta}$ , is also known since we have already found the concentrations at the triple junction. The procedure of calculation of  $\kappa(0)$  is straightforward but tedious and involves new thermodynamical parameters. Therefore, we explain this procedure only schematically: The concentrations in the solid phases at the triple junction can be calculated, on one hand, using the condition of local equilibrium with the liquid phase (along the  $x_{\alpha(\beta)}$  interface) and, on the other hand, using the condition of local equilibrium between two solid phases (along the  $x_{\alpha\beta}$  interface). At the triple junction these compositions should coincide. The capillary corrections to the equilibrium solid concentrations

can be written similar to Eq. (2) for all there interfaces. Since the profiles  $x_{\alpha}$  and  $x_{\beta}$  have been already found, the mentioned continuity condition allows to calculate the curvature  $\kappa(0)$  of the solid-solid interface.

We note, however, that the term  $\kappa(0)/q$  in Eq. (21) is of order  $\theta(D_{\alpha\beta}\Delta/D)^{1/3}$  and can be neglected compared to  $\theta$  for small  $\Delta$ . This means that the tedious calculations explained above are not needed in the limit of small  $\Delta$ . We also note that the characteristic length scales of the solid-solid interfacial pattern are small compared to the characteristic length scales of the melt structures by the same small parameter  $(D_{\alpha\beta}\Delta/D)^{1/3}$ . Moreover, the diffusional flux along the solid-solid interface has a nonzero value at the triple junction. In principal, this flux has to be taken into account in the description of the diffusional field in the liquid phase. This effect has been neglected in the previous sections. More careful analysis shows that corrections to Eq. (6) due to this effects are small by the same small parameter,  $(D_{\alpha\beta}\Delta/D)^{1/3} << 1$ . Thus, in the limit of small  $\Delta$  the surface diffusion process has no influence on the kinetics of the contact melting and allows only for the necessarily adjustment of the solid-solid interface inside the relatively small region in the vicinity of the triple junction.

#### V. CONCLUSION

We have developed and analyzed a relatively simple model for the melting kinetics along the solid-solid interphase boundaries in eutectic and peritectic systems. The process is controlled by the diffusion inside the liquid phase and the existence of the triple junction is crucial for the velocity selection problem. The additional assumption of small opening angles  $\varphi$  at the triple junction plays only a technical role and allows to solve the posed problem essentially analytically using the lubrication approximation for the diffusion field in the liquid phase. The obtained scaling results for the dependence of the steady-state velocity of the moving pattern on the overheating, which are exact in the limit of small angles, can still be used for the moderate values of the angles with only prefactors of the order of unity missing. We note the obtained scaling relation,  $v \sim D\Delta^2/d$ , is similar to the scaling relation in eutectic growth. Using Eq. (15) and characteristic values of the parameters  $D \sim 10^{-9}m^2/s$ ,  $d \sim 10^{-9}m$ ,  $\Delta \sim 10^{-3}$  and  $\theta \sim 1$  we estimate the characteristic velocity to be of the order of  $v \sim 10^{-6}m/s$ . We hope that our results will stimulate some new model experiments on contact melting phenomena.

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